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(54) Curable epoxide resin mixtures
and their use in corrosion resistant
coatings

(57) The mixtures can contain various
epoxide resins and curing agents

contained in the mixtures are in
particular novolacs, which contain not
less than 3 phenolic OH groups and no
functional groups of any other type
apart from these, or reaction products
of glyoxal or acrolein with phenol.

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SPECIFICATION

Curable epoxide resin mixtures and their use

The invention relates to curable epoxide resin mixtures which are particularly suitable for coating steel sheets to protect them against corrosion.

Epoxide resin/curing agent combinations for protection against corrosion under severe conditions have already been known for a relatively long time. In this connection reference should be made, for example, to U.S. Patent Specification 3,019,202 and German Offenlegungsschrift 2,505,278. The curable mixtures according to U.S. Patent 3,019,202 contain diepoxysulfone compounds as the epoxide resins. The curing agents contained in these mixtures can be, inter alia, monomeric polyphenols, such as bis-(4-hydroxyphenyl)-2,2-propane, pyrogallol and resorcinol. However, the curable mixtures of this prior art have considerable disadvantages. In particular, very long stoving or curing times are required. It is not possible to obtain satisfactory curing at temperatures below 160°C. However, in view of the energy costs, short stoving times and low stoving temperatures are desirable.

The layer thicknesses obtainable with this process of the prior art are so small that 3 to 7 coatings are required to obtain a total layer thickness of about 100 to 150 µm. However, with these known systems a minimum layer thickness of this magnitude is required in every case if it is desired to obtain effective protection against corrosion. Multiple coating of this type coupled with relatively large final coating thicknesses is uneconomical from the point of view of both time and material.

German Offenlegungsschrift 2,505,278 relates to steel sheets coated with synthetic resin. The coating systems described in this publication are epoxide resin mixtures which contain thermosetting phenolic resins as the curing agent. Phenolic resins of this type, for example resol resins, already have considerable molecular weights and in addition to phenolic OH groups also contain yet further functional groups, for example methylol groups. The synthetic resin systems described in German Offenlegungsschrift 2,505,278 have virtually the same disadvantages as the systems described in the U.S. patent discussed above. Both of the known systems also result in coatings which are not sufficiently stable with regard to several aggressive liquids. These liquids are acetic acid solutions with a concentration of 50% or higher, concentrated hydrochloric acid, nitric acid and ammonia solutions.

The object of the invention is to provide curable epoxide resin mixtures which are suitable for the production of corrosion-resistant coatings on steel sheets or other substrates and which do not have the disadvantages of the known systems, which have been discussed. Thus, it should be possible to use shorter stoving times and lower stoving temperatures for curing the mixtures. Coatings of adequate thickness which have an anti-corrosive effect which is even superior to that of the thicker multi-layer coatings of known systems should already be achieved with the first coating when coating the steel sheets.

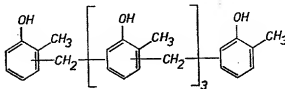
The invention relates to curable epoxide resin mixtures containing a) one or more epoxide resins which are based on bisphenol A and/or bisphenol F and have an epoxide content of 0.3 to 2.0 equivalents/kg, and/or b) one or more epoxide resins which are based on bisphenol A and/or bisphenol F and/or phenol novolac or an alkylphenol novolac and have an epoxide content of 2.0 to 8.0 equivalents/kg and/or c) one or more hydrogenated bisphenol A glycidyl ethers and/or hydantoin epoxide resins and/or polyglycidyl esters with an epoxide content of 4.0 to 8.0 equivalents/kg, d) 10 to 100% by weight, based on the sum of the epoxide resins listed under a) to c), of one or more curing agents of the type comprising polyphenols and/or oligophenols which contain not less than 3 phenolic OH groups and no functional groups of any other type apart from these and e) 0.2 to 3.0% by weight, based on the sum of the epoxide resins listed under a) to c), of one or more curing accelerators and, if desired, additionally containing f) conventional assistants and additives for lacquers and/or g) organic solvents.

Preferred curable epoxide resin mixtures are those containing a) one or more epoxide resins which are based on bisphenol A and/or bisphenol F and have an epoxide content of 0.3 to 2.0 equivalents/kg and/or b) one or more epoxide resins which are based on bisphenol A and/or bisphenol F and/or phenol novolac or an alkylphenol novolac and have an epoxide content of 2.0 to 6.0 equivalents/kg and/or c) one or more hydrogenated bisphenol A glycidyl ethers and/or hydantoin epoxide resins and/or polyglycidyl esters with an epoxide content of 4.0 to 8.0 equivalents/kg, d) 10 to 40% by weight, based on the sum of the epoxide resins listed under a) to c), of one or more curing agents of the type comprising polyphenols and/or oligophenols which contain not less than 3 phenolic OH groups and no functional groups of any other type apart from these and e) 0.2 to 3.0% by weight, based on the sum of the epoxide resins listed under a) to c), of one or more curing accelerators and, if desired, additionally containing f) conventional assistants and additives for lacquers and/or g) organic solvents.

The curing agents (d) which are of the type comprising polyphenols and/or oligophenols containing not less than 3 phenolic OH groups and no functional groups of any other type apart from these and are contained in the mixtures according to the invention are preferably those of the group comprising phenol novolacs, cresol novolacs, bisphenol A novolacs, bisphenol F novolacs, reaction products of 1 mol of glyoxal with 4 mols of phenol and reaction products of 1 mol of acrolein with 3 mols of phenol. The curing accelerators (e) which are contained in the mixtures are preferably those of

the group comprising the Sn-organic compounds, the imidazole derivatives and the 4-dialkyl-aminopyridines.

A preferred embodiment of the invention comprises those mixtures which consist of a) 30 to 50 parts by weight of one or more epoxide resins which are based on bisphenol A and/or bisphenol F and have an epoxide content of 0.5 to 2.0 equivalents/kg, b) 50 to 70 parts by weight of one or more epoxide resins which are based on bisphenol A and/or bisphenol F and/or phenol novolac or an alkylphenol novolac and have an epoxide content of 2.0 to 4.0 equivalents/kg, d) 25 to 35% by weight, based on the sum of the epoxide resins listed under a) and b), of cresol novolac of the approximate formula I



and e) 0.2 to 1.0% by weight, based on the sum of the epoxide resins listed under a) and b), of one or more accelerators from the group comprising imidazole, 4-dimethylaminopyridine and tin octoate and, if desired, additionally f) 0.5 to 2% by weight, based on the epoxide resins and curing agent, of levelling agents and g) solvents from the group comprising ethylglycol acetate, methyl isobutyl ketone and xylene.

Mixtures which contain merely a semi-solid to solid bisphenol A epoxide resin as the epoxide compound and merely a cresol novolac of the formula I as the curing agent (d), the ratio being so chosen that there is 1 (±30%) epoxide group per phenolic OH group, are also a further preferred embodiment of the invention.

A particular embodiment of the invention comprises those mixtures which consist of a) 10 to 100 parts by weight of one or more epoxide resins which are based on bisphenol A and/or bisphenol F and have an epoxide content of 0.3 to 6.0 equivalents/kg, b) 0 to 100 parts by weight of one or more epoxide resins which are based on phenol novolac or an alkylphenol novolac and have an epoxide content of 3.0 to 8.0 equivalents/kg, c) 0 to 100 parts by weight of one or more hydantoin epoxide resins and/or polyglycidyl esters with an epoxide content of 4.0 to 8.0 equivalents/kg, d) 10 to 100% by weight, based on the sum of the epoxide resins listed under a) to c), of one or more curing agents of the type comprising polyphenols and/or oligophenols which contain not less than 3 phenolic OH groups and no functional groups of any other type apart from these and e) 0.2 to 3.0% by weight, based on the sum of the epoxide resins listed under a) to c), of one or more curing accelerators and, if desired, additionally f) conventional assistants and additives for lacquers, which mixtures are in the form of powders, the individual particles being homogeneous particles of the total mixture, and do not contain any epoxide resins listed under a), b) and c) which are liquid or any solvents, or contain liquid epoxide resin and/or solvents only in amounts such that the powders are non-tacky and free-flowing.

Preferred mixtures are pulverulent mixtures consisting of a) 10 to 100 parts by weight of one or more epoxide resins which are based on bisphenol A and/or bisphenol F and have an epoxide content of 0.3 to 6.0 equivalents/kg, b) 0 to 100 parts by weight of one or more epoxide resins which are based on phenol novolac or an alkylphenol novolac and have an epoxide content of 3.0 to 8.0 equivalents/kg, c) 0 to 100 parts by weight of one or more hydantoin epoxide resins and/or polyglycidyl esters with an epoxide content of 4.0 to 8.0 equivalents/kg, d) 10 to 40% by weight, based on the sum of the epoxide resins listed under a) to c), of one or more curing agents of the type comprising polyphenols and/or oligophenols which contain not less than 3 phenolic OH groups and no functional groups of any other type apart from these and e) 0.2 to 3.0% by weight, based on the sum of the epoxide resins listed under a) to c), of one or more curing accelerators and, if desired, additionally f) conventional assistants and additives for lacquers, which mixtures are in the form of powders, the individual particles being homogeneous particles of the total mixture, and do not contain any epoxide resins listed under a), b) and c) which are liquid or any solvents, or contain liquid epoxide resin and/or solvents only in amounts such that the powders are non-tacky and free-flowing.

A preferred embodiment of these special pulverulent mixtures comprises those which consist of a) 10 to 100 parts by weight of one or more epoxide resins which are based on bisphenol A and/or bisphenol F and have an epoxide content of 0.3 to 6.0 equivalents/kg, b) 0 to 100 parts by weight of one or more epoxide resins which are based on phenol novolac or an alkylphenol novolac and have an epoxide content of 3.0 to 8.0 equivalents/kg, d) 15 to 30% by weight, based on the sum of the epoxide resins listed under a) and b), of one or more curing agents of the type comprising polyphenols and/or oligophenols which contain not less than 3 phenolic OH groups and no functional groups of any other type apart from these and e) 0.2 to 3.0% by weight, based on the sum of the epoxide resins listed under a) and b), of one or more curing accelerators and, if desired, additionally f) conventional assistants and additives for lacquers, which mixtures are in powder form, the individual particles being homogeneous

particles of the total mixture, and do not contain any epoxide resins listed under a) and b) which are liquid or any solvents, or contain liquid epoxide resins and/or solvents only in amounts such that the powders are non-tacky and free-flowing.

- 5 The pulverulent mixtures according to the invention can also be suspended in water or in an organic solvent which does not dissolve the mixture, or in a mixture thereof, the solids concentration being 15 to 50% by weight, based on the total suspension. 5

The mixtures according to the invention can contain all or some of one or more of the epoxide resins listed under a), b) and c) and all or some of one or more of the curing agents listed under d) in the form of preadducts (reaction products of epoxide resin and curing agent). The adducts which 10 fundamentally are possible are given in the list below [a), b), c) and the like are to be understood as meaning the products which are indicated under these letters in the above mixtures]. 10

a) and b) adduct with d)

a) adduct with d)

b) adduct with d)

- 15 a) and c) adduct with d) 15

c) adduct with d)

b) and c) adduct with d)

a) and b) and c) adduct with d).

- 20 The epoxide resins contained in the mixtures according to the invention have been known for a long time and frequently described in the literature, so that a more detailed description thereof is superfluous. This also applies analogously in the case of the curing agents containing not less than 3 phenolic OH groups and no functional groups of any other type apart from these, such as the novolacs and the reaction products of glyoxal or acrolein with phenol. Such products are obtained by a condensation reaction in an acid medium. With regard to these curing agents, reference should be made to the literature on modern phenolic resin chemistry. 25

- Assistants and additives which can be contained in the mixtures according to the invention are in particular fillers, pigments, dyes, modifiers, agents imparting flexibility, plasticisers and levelling agents. Known levelling agents are, for example, polyvinylbutyral, carbanic acid ester resins and specific polyacrylates. These auxiliary substances are also described comprehensively in the literature (thus, for example, in the "Handbook of Epoxy Resins" by H. Lee and K. Neville, Mc Graw-Hill Book Comp. (1967)). The same also applies, moreover, in the case of the organic solvents, which can be contained in the mixtures according to the invention, and likewise in the case of the curing accelerators. 30

- The invention also relates to the use of the mixtures according to the invention for the production of acid-resistant, alkali-resistant and ammonia-resistant coatings for metals, especially for steel sheets. 35 The invention can be used, inter alia, in acid-proof construction, for priming in vehicle building and for the internal lacquer coating of packaging, vats and containers, including cans for foodstuffs and drinks.

- If a liquid mixture according to the invention (lacquer solution) is used for the production of a corrosion-resistant coating of this type, the liquid mixture is first applied to the steel sheet, for example by the dipping, spreading or rolling process but preferably by means of a conventional lacquer spray gun. Drying and curing at temperatures of $\leq 130^\circ\text{C}$ are then carried out. 40

- The mixtures according to the invention which are solvent-free or have a low solvent content are employed, when used according to the invention, either in the dry form as powder-coating lacquers or alternatively as suspensions in water or inert solvents. In the former case, the powder is applied by known powder-coating methods, such as whirl-sintering or flame-spraying or by dispersing by means of an electrostatic powder-spraying installation. When a suspension of the powder is used, this is applied most simply by the use of a lacquer spray gun. In both cases application is in this case also followed by curing at not less than 130°C , preceded by drying if necessary. 45

The invention is illustrated in more detail in the examples which follow. In these examples parts are always by weight unless expressly defined otherwise.

50 EXAMPLE 1 50

(Epoxide resin/cresol novolac lacquer system)

- 65 g of a polyglycidyl ether which is semi-solid at room temperature, has been prepared by a condensation reaction of bisphenol A with epichlorohydrin in the presence of alkali and has an epoxide content of 4.0 equivalents/kg are mixed with 35 g of a polyglycidyl ether which is solid at room temperature, has been prepared by a condensation reaction of bisphenol A with epichlorohydrin in the presence of alkali and has an epoxide content of 0.5 equivalent/kg and this mixture is dissolved at 55

80—100°C in a 1:1 mixture of ethylglycol acetate/xylene to give a 50% solution. 34 g of a cresol novolac with a OH content of 8.25 equivalents/kg (molar ratio of cresol-formaldehyde during the preparation = 1:0.7), which has been dissolved at 60—80°C in 22 g of methyl isobutyl ketone and then cooled to room temperature, are then added to the epoxide resin solution which has been cooled to room temperature. 0.8 g of a mixture of 0.4 g of tin octoate and 0.4 g of dimethylaminopyridine is added as a reaction accelerator.

The viscosity of the lacquer thus obtained is adjusted to about 150 mPa s/25°C using methyl isobutyl ketone and the lacquer is applied to a steel substrate using a conventional spray gun. The thickness of the dry film after stoving the lacquer (20 minutes at 130°C to 20' at 160°C) is about 50 µm. The characteristics of the film thus obtained are summarised in Table 1.

EXAMPLE 2

(Epoxide resin/polyphenol lacquer systems)

76 g of a bisphenol A glycidyl ether (preparation as described in Example 1) which is semi-solid at room temperature and has an epoxide content of 2.5 equivalents/kg are mixed with 24 g of a bisphenol A glycidyl ether (preparation as described in Example 1) which is solid at room temperature and has an epoxide content of 0.5 equivalent/kg and this mixture is dissolved in a 1:1 mixture of ethylglycol acetate/xylene to give a 50% solution. 22 g of a polyphenol, which has been prepared by reaction 3 mols of phenol with 1 mol of acrolein and has a hydroxyl content of 9.35 equivalents/kg and has been dissolved at 60—80°C in 15 g of methyl isobutyl ketone and then cooled to room temperature, are then added to the epoxide resin solution, which has been cooled to room temperature. 0.6 g of a mixture of 0.3 g of tin octoate and 0.3 g of dimethylaminopyridine is added as a reaction accelerator.

The viscosity of the lacquer prepared in this way is adjusted to about 150 mPa s/25°C using methyl isobutyl ketone and the lacquer is applied to a steel substrate using a conventional spray apparatus. The thickness of the dry film after stoving the lacquer (20 minutes at 130°C—160°C) is about 50 µm. The characteristics of the lacquer film are again given in Table 1.

Data with regard to the test methods (Substrate: sheet steel)

P = Persoz pendulum hardness; 40—50 µm thick film measured at 20°C and 65% relative humidity (RH). The hardness is given in seconds (French Standard: AFNOR NFT 30,016). Apparatus: type 300 from Erichsen (Federal Republic of Germany).

E = Erichsen deep-drawing according to DIN 53156, measured on 40—50 µm thick films at 20°C and 65% RH. Quoted in mm.

I = Impact test, impact on the film; film thickness 40—50 µm. Weight of the test hammer 1 kg; diameter of the hemisphere making impact: 2 cm. Test temperature 20°C at 65% RH.

RI = Reverse impact test, impact on the substrate (sheet steel); film thickness 40—50 µm; weight of the test hammer 1 kg; diameter of the hemisphere making impact: 2 cm. Test temperature 20°C at 65% RH.

M = Mandrel bending test, 8 mm mandrel at 20°C and 65% RH; film thickness 40—50 µm (DIN 53 152).

Ac = Acetone rubbing test. 20 strokes backwards and forwards with cottonwool moistened with acetone on the cured film. Film thickness 40—50 µm. Test temperature 20°C at 65% RH. Evaluation matched to DIN 53 230.

BW = Boiling water test; 6 hours at 96°C on 40—50 µm thick films. Evaluation matched to DIN 53 230.

Cr = Cross-hatch test DIN 53 151 using cutting apparatus A. Film thickness 40—50 µm. Test temperature 20°C, 65% RH.

Ch = Test to determine the stability to chemicals, carried out on films with a film thickness of about 100 µm (2-layer application); curing 2 x 20' at 130°C or 2 x 20' at 160°C. Immersion temperature 20—22°C. The stability is assessed visually, the following 3 possibilities exist:

+ = Film is stable to the test medium and is unchanged after completion of the test (1 month).

A = Film has limited stability to the test medium, i.e. is stable only for a short time. Slight damage such as swelling and softening arises during the 1-month test. The substrate (sheet steel) is protected.

D = Film is destroyed, i.e. protection of the substrate by the paint is no longer ensured; the test medium has contact with the substrate.

TABLE 1

Example No.	1		2	
Type of resin mixture	Epoxide resin/ cresol novolac		Epoxide resin/ polyphenol	
Curing conditions	20°, 130°C	20°, 160°C	20°, 130°C	20°, 160°C
(P) Persoz hardness (seconds)	390	380	395	365
(E) Erichsen test (mm)	7.5	7.0	8.5	8.0
(I) Impact test (cmkg)	90	90	90	90
(RI) Reverse impact (cmkg)	90	90	90	90
(M) Mandrel bending test (ϵ°)	180	180	180	180
(Ac) Acetone rubbing test	0	0	1	1
(BW) Boiling water test	0	0	0	0
(Cr) Cross-hatch test	1	1	2	1
Stability to deionised water	+	+	+	+
25% ammonia:	+	+	+	+
50% acetic acid	+	+	A	+
70% sulfuric acid	+	+	+	+
36% hydrochloric acid	+	+	+	+
20% nitric acid	+	+	+	+
methanol	D	A	D	D
toluene	D	+	D	+

EXAMPLE 3 TO 20

The procedure of Example 1 is repeated, except that the following epoxide resins and curing agents are used:

- 5 Epoxide resin type 1: Semi solid bisphenol A epoxide resin with an epoxide content of 3.6—4.0 equivalents/kg. 5
- Epoxide resin type 2: Solid bisphenol A epoxide resin with an epoxide content of 2.3—2.6 equivalents/kg.
- 10 Epoxide resin type 3: Liquid bisphenol F epoxide resin with a viscosity of 5,000—8,000 mPa s/25°C and an epoxide content of 5.6—6.0 equivalents/kg. 10
- Epoxide resin type 4: Semi-solid cresol novolac epoxide resin with an epoxide content of 4.8—5.2 equivalents/kg.
- Epoxide resin type 5: Liquid bisphenol H epoxide resin (i.e. completely hydrogenated bisphenol A epoxide resin) with a viscosity of 2,000—3,000 mPa s/25°C and an epoxide content of 4.2—4.6 equivalents/kg. 15
- 15 Epoxide resin type 6: Liquid hydantoin epoxide resin with a viscosity of 1,500—2,000 mPa s/25°C and an epoxide content of 7—7.5 equivalents/kg. 15
- Epoxide resin type 7: Liquid diglycidyl tetrahydrophthalate with a viscosity of 400—700 mPa s/25°C and an epoxide content of 6.1—6.5 equivalents/kg.
- 20 Polyphenol I: (The same as in Example 2) reaction product of 1 mol of acrolein and 3 mols of phenol, with a hydroxyl content of 9.35 equivalents/kg. 20
- Polyphenol II: Reaction product of glyoxal and 4 mols of phenol, with a hydroxyl content of 10.05 equivalents/kg.
- 25 Cresol novolac III: (as in Example 1) with a hydroxyl content of 8.25 equivalents/kg. 25
- The viscosity of the lacquers produced is adjusted to about 150 mPa s/25°C by means of methyl

isobutyl ketone, using the method described in Example 1, and the lacquers are applied to a steel substrate by means of a conventional spray apparatus. The thickness of the dry film after stoving the lacquer (20 minutes at 130°C—160°C) is about 50 μm .

The test values of the resulting film coatings are listed in Table 2.

TABLE 2

Example No.	g of epoxide resin	Type of epoxide resin	g of poly-phenol I	g of poly-phenol II	g of novolac III	g of acetal-erator	Curing conditions (20 minutes)	P sec.	E mm	I omkg	RI omkg	M $\frac{1}{2}$	Ac	BW	Cr
3	100	1			48	2	100°C	280	7.0	90	20	180	1	0	2
4	100	2	27			2	130°C	360	4.5	90	90	60	0	0	2
5	100	2		25		2	160°C	360	5.5	90	70	180	0	0	4
6	100	2			30	2	160°C	330	7.0	90	70	70	0	0	4
7	100	3	82			1.5	130°C	350	3.0	90	90	180	0	0	4
8	100	3			72	1.5	160°C	360	4.0	90	50	100	0	0	4
9	100	4	52			2	130°C	300	4.8	90	20	100	0	0	4
10	100	4			60	2	130°C	310	3.0	70	10	40	0	0	4
11	100	5	45			1.5	160°C	330	7.0	90	50	180	0	0	1
12	100	5			53	1.5	160°C	360	8.5	80	20	90	0	0	1
13	100	8	76			1.5	130°C	320	7.0	90	20	180	0	0	2
14	100	6			88	1.5	160°C	340	5.5	90	20	60	0	0	3
15	100	7	68			1.5	150°C	370	7.5	90	90	180	0	0	3
16	100	7			77	1.5	130°C	390	7.0	90	50	180	0	0	4
17	100	2	19			2	150°C	380	5.0	90	90	180	0	0	2
18	100	2	34			2	180°C	340	8.0	90	90	180	0	0	2
19	100	1			34	2	130°C	320	5.0	90	50	150	0	0	4
20	100	1			62	2	130°C	300	7.5	90	80	60	0	0	4

EXAMPLE 21

Powder-coating method)

- 87 parts of a bisphenol A epoxide resin with an epoxide content of 1.3 equivalents/kg, 12.5 parts of a reaction product of 1 mol of acrolein and 3 mols of phenol, 25 parts of TiO_2 , 25 parts of BaSO_4 as a filler, 0.25 part of imidazole and 0.7 part of a levelling agent of the polyvinylbutyral type (Modaflow® from Monsanto) are mixed together and the mixture is homogenised in a Ko-kneader (from Buss) at temperatures between 30 and 100°C and cooled to room temperature. The cooled product is ground to a fineness of grain of $\leq 100 \mu\text{m}$ and applied in a known manner by means of an electrostatic powder-spraying installation to diverse sample metal sheets. After a curing time of 20 minutes at 150°C, homogeneous, pore-free films with good levelling and high stability to mechanical stress and chemicals are obtained.

EXAMPLE 22

(Use of a powder suspension)

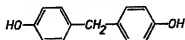
- 50 parts of a bisphenol A epoxide resin with an epoxide content of 1.3 equivalents/kg, 11 parts of a bisphenol F novolac with an epoxide content of 120 equivalents/kg, based on the phenolic OH groups, and a melting point of 85—90°C, 31 parts of TiO_2 , 0.6 part of imidazole and 0.9 part of the levelling agent used in Example 21 are mixed, homogenised and processed to a powder with an average particle size of $\leq 100 \mu\text{m}$, as in Example 21.

- 35 parts of this powder are suspended in 65 parts of water and ground in a bead mill to a particle size of about 10 μm . The suspension thus obtained is applied to sample metal sheets using a conventional lacquer spray gun and the coatings are stoved for 20 minutes at 150°C. Homogeneous, pore-free films with good levelling and good chemical and mechanical properties form.

EXAMPLES 23 TO 30

- The procedure is as in Example 1. The following epoxide resins and curing agents are additionally used:
- Epoxide resin type 8: Solid bisphenol A epoxide resin with an epoxide content of 0.5 equivalent/kg; corresponds to the solid resin mentioned in Examples 1 and 2.
- Bisphenol F novolac: Condensation product obtained from phenol and formaldehyde and having the formula

30



(semi-solid) 30

Hydroxyl content: 10.0 equivalents/kg.

Phenol novolac: Condensation product obtained from phenol and formaldehyde but with a higher molecular weight than bisphenol F. The main constituent is trifunctional as in the cresol novolac. Solid product with a hydroxyl content of 9.9 equivalents/kg.

- Bisphenol A novolac: Condensation product obtained from bisphenol A and formaldehyde (solid). Hydroxyl content 8.25 equivalents/kg.

- The viscosity of the lacquers produced is adjusted to about 150 mPa s/25°C by means of methyl isobutyl ketone, using the method described in Example 1, and the lacquers are applied to a steel substrate by means of a conventional spray apparatus. The thickness of the dry film after stoving the lacquer (20 minutes at 130°C—160°C) is about 50 μm .

The compositions of the mixtures of Examples 23 to 30 and the curing conditions for these mixtures are listed in Table 3, and the test values for the resulting film coatings are listed in Table 4.

TABLE 3

Example No.	100 g of epoxide resin mixture		Cresol novolac (g)	Bisphenol F novolac (g)	Phenol novolac (g)	Bisphenol A novolac (g)	Imidazole accelerator (g)	Curing 20', at
	g	Type						
23	40	2	32				1	130°C
	40	6						160°C
	20	6						130°C
24	70	8	28				1	160°C
	80	7						130°C
25	70	2	47				1	160°C
	30	6						130°C
26	70	2	44				1	160°C
	30	7						130°C
27	40	8	38				1	160°C
	60	4						130°C
28	65	1		29			1	160°C
	35	8						130°C
29	65	1			29		1	160°C
	35	8						130°C
30	65	1				34	1	160°C
	35	8						130°C

TABLE 4

Example No.	P sec.	E mm	I cm/kg	RI cm/kg	M °	Ac	BW	Cr	20 minutes curling at
23	290	6,5	90	90	180	1	4	2	130°C
	290	7,5	90	90	180	0	4	1	160°C
24	330	8,5	90	90	180	3	4	1	130°C
	330	9,0	90	90	180	2	4	1	160°C
25	320	5,0	90	90	180	0	4	2	130°C
	320	6,5	90	90	180	0	4	5	160°C
26	320	7,5	90	40	180	0	4	5	130°C
	280	7,0	90	90	180	0	4	1	160°C
27	310	7,0	90	40	180	0	0	3	130°C
	310	5,0	90	50	180	0	0	3	160°C
28	290	9,5	70	80	90	3	0	2	130°C
	270	9,5	90	90	180	3	0	2	160°C
29	300	9,0	90	90	180	2	0	1	130°C
	310	9,0	90	90	180	2	0	1	160°C
30	310	8,0	90	70	180	1	0	2	130°C
	300	8,0	90	90	180	0	0	4	160°C

EXAMPLE 31

(Preparation of the pre-adduct I)

290 g of the cresol novolac are dissolved in a sulfonation flask in 290 g of methyl isobutyl ketone under gentle reflux. 240 g of a separately prepared 50% solution of epoxide resin type 1 in methyl isobutyl ketone are then added to the clear solution. The mixture is boiled under gentle reflux until the reaction product has an epoxide content of < 0.005 equivalent/kg. 0.5% by weight of imidazole, based on the total mixture, is added to accelerate the reaction. The solution has a viscosity of about 8,000 mPa s/25°C and a OH equivalent of 2.4 equivalents/kg.

EXAMPLE 32

(Preparation of the pre-adduct II)

290 g of the cresol novolac are dissolved in a sulfonation flask in 590 g of methyl isobutyl ketone under gentle reflux. 300 g of the solid epoxide resin type 8 are then added to the clear solution and the mixture is boiled under gentle reflux until the epoxide content of the solution < 0.005 equivalent/kg. 0.5% by weight of imidazole, based on the total mixture, is added to accelerate the reaction. The solution has a viscosity of about 2,000 mPa s/25°C and a OH equivalent of 1.9 equivalents/kg.

The mixtures prepared using the pre-adducts I and II and the test values of the resulting film coatings are listed in Table 5.

TABLE 5

Example No.	31		32	
Epoxide resin type 1 (g)	60		100	
Epoxide resin type 8 (g)	40			
Pre-adduct I (50%) (g)	112			
Pre-adduct II (50%) (g)			212	
Imidazole (% by weight)	0.5		0.5	
Solvent (g)	236		168	
Viscosity (mPa s)	110		110	
Solids content (% by weight)	35		43	
Curing for 20 minutes at	130 °C	160 °C	130 °C	160 °C
(P) Persoz hardness (seconds)	330	360	400	390
(E) Erichsen test (mm)	7.5	5.5	8.0	7.5
(I) Impact test (cmkg)	90	90	90	90
(RI) Reverse impact (cmkg)	90	60	50	90
(M) Mandrel bending test ($\frac{1}{4}$ ")	180	180	180	180
(Ac) Acetone rubbing test	1	0	2	0
(BW) Boiling water test	0	1	0	0
(Cr) Cross-hatch	1	1	1	1

Table 6 lists the stability to chemicals of the formulations from Table 5 after immersion for 6 months at 20—22°C. (Curing: 20 minutes at 160°C).

TABLE 6

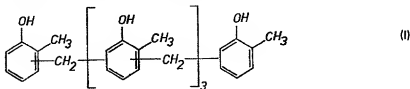
Example No.	31	32
deionised water	stable	stable
synthetic seawater	stable	stable
30% sodium hydroxide solution	stable	stable
25% ammonia	stable for 5 months	stable for 1 month
50% acetic acid	stable	stable
70% sulfuric acid	stable	stable for 4 months
20% hydrochloric acid	stable	stable
36% hydrochloric acid	stable	stable for 4 months
20% nitric acid	stable	stable
toluene	stable	stable for 2 months
methanol	softens not stable	not stable

CLAIMS

1. A curable epoxide resin mixture containing a) one or more epoxide resins which are based on bisphenol A and/or bisphenol F and have an epoxide content of 0.3 to 2.0 equivalents/kg, and/or b) one or more epoxide resins which are based on bisphenol A and/or bisphenol F and/or phenol novolac or an alkylphenol novolac and have an epoxide content of 2.0 to 6.0 equivalents/kg and/or c) one or more hydrogenated bisphenol A glycidyl ethers and/or hydantoin epoxide resins and/or polyglycidyl esters with an epoxide content of 4.0 to 8.0 equivalents/kg, d) 10 to 100% by weight, based on the sum of the epoxide resins listed under a) to c), of one or more curing agents of the type comprising polyphenols and/or oligophenols which contain not less than 3 phenolic OH groups and no functional groups of any other type apart from these and e) 0.2 to 3.0% by weight, based on the sum of the epoxide resins listed under a) to c), of one or more curing accelerators and, if desired, additionally containing f) conventional assistants and additives for lacquers and/or g) organic solvents.
2. A curable epoxide resin mixture containing a) one or more epoxide resins which are based on bisphenol A and/or bisphenol F and have an epoxide content of 0.3 to 2.0 equivalents/kg and/or b) one or more epoxide resins which are based on bisphenol A and/or bisphenol F and/or phenol novolac or an alkylphenol novolac and have an epoxide content of 2.0 to 6.0 equivalents/kg and/or c) one or more hydrogenated bisphenol A glycidyl ethers and/or hydantoin epoxide resins and/or polyglycidyl esters with an epoxide content of 4.0 to 8.0 equivalents/kg, d) 10 to 40% by weight, based on the sum of the epoxide resins listed under a) to c), of one or more curing agents of the type comprising polyphenols and/or oligophenols which contain not less than 3 phenolic OH groups and no functional groups of any other type apart from these and e) 0.2 to 3.0% by weight, based on the sum of the epoxide resins listed under a) to c), of one or more curing accelerators and, if desired, additionally containing f) conventional assistants and additives for lacquers and/or g) organic solvents.
3. A mixture according to claim 1 or 2, which contains, as the curing agent or agents (d) of the type comprising polyphenols and/or oligophenols which contain not less than 3 phenolic OH groups and no functional groups of any other type apart from these, a curing agent or agents from the group comprising phenol novolacs, cresol novolacs, bisphenol A novolacs, bisphenol F novolacs, reaction products of 1 mol of glyoxal with 4 mols of phenol and reaction products of 1 mol of acrolein with 3 mols of phenol.
4. A mixture according to any of Claims 1 to 3, which contain, as the curing accelerator or accelerators (e), a curing accelerator or curing accelerators from the group comprising the Sn-organic compounds, the imidazole derivatives and the 4-dialkylaminopyridines.
5. A mixture according to any preceding claim, which contains all or some of one or more of the epoxide resins listed under a), b) and c) and all or some of one or more of the curing agents listed under

d) in the form of pre-adducts (reaction products of epoxide resin and curing agent).

6. A mixture according to claim 1, which is composed of a) 30 to 50 parts by weight of one or more epoxide resins which are based on bisphenol A and/or bisphenol F and have an epoxide content of 0.5 to 2.0 equivalents/kg, b) 50 to 70 parts by weight of one or more epoxide resins which are based on bisphenol A and/or bisphenol F and/or phenol novolac or an alkylphenol novolac and have an epoxide content of 2.0 to 4.0 equivalents/kg, d) 25 to 35% by weight, based on the sum of the epoxide resins listed under a) and b), of cresol novolac of the approximate formula I



and e) 0.2 to 1.0% by weight, based on the sum of the epoxide resins listed under a) and b), of one or more accelerators from the group comprising imidazole, 4-dimethylaminopyridine and tin octoate and, if desired, additionally f) 0.5 to 2.0% by weight, based on the epoxide resins and curing agent, of levelling agents and g) solvents from the group comprising ethylglycol acetate, methyl isobutyl ketone and xylene.

7. A mixture according to claim 6, which contains merely a semi-solid to solid bisphenol A epoxide resin as the epoxide compound and merely a cresol novolac of the formula I as the curing agent (d), the ratio being so chosen that there is 1 (±30%) epoxide group per phenolic OH group.

8. A mixture according to claim 1, which is composed of a) 10 to 100 parts by weight of one or more epoxide resins which are based on bisphenol A and/or bisphenol F and have an epoxide content of 0.3 to 6.0 equivalents/kg, b) 0 to 100 parts by weight of one or more epoxide resins which are based on phenol novolac or an alkylphenol novolac and have an epoxide content of 3.0 to 6.0 equivalents/kg, c) 0 to 100 parts by weight of one or more hydantoin epoxide resins and/or polyglycidyl esters with an epoxide content of 4.0 to 8.0 equivalents/kg, d) 10 to 100% by weight, based on the sum of the epoxide resins listed under a) to c), of one or more curing agents of the type comprising polyphenols and/or oligophenols which contain not less than 3 phenolic OH groups and no functional groups of any other type apart from these and e) 0.2 to 3.0% by weight, based on the sum of the epoxide resins listed under a) to c), of one or more curing accelerators and, if desired, additionally f) conventional assistants and additives for lacquers, wherein the said mixture is in the form of a powder, the individual particles being homogeneous particles of the total mixture, and does not contain any epoxide resins listed under a), b) and c) which are liquid or any solvents, or contains liquid epoxide resin and/or solvents only in amounts such that the powder is non-tacky and free-flowing.

9. A mixture according to claim 8, which is composed of a) 10 to 100 parts by weight of one or more epoxide resins which are based on bisphenol A and/or bisphenol F and have an epoxide content of 0.3 to 6.0 equivalents/kg, b) 0 to 100 parts by weight of one or more epoxide resins which are based on phenol novolac or an alkylphenol novolac and have an epoxide content of 3.0 to 6.0 equivalents/kg, c) 0 to 100 parts by weight of one or more hydantoin epoxide resins and/or polyglycidyl esters with an epoxide content of 4.0 to 8.0 equivalents/kg, d) 10 to 40% by weight, based on the sum of the epoxide resins listed under a) to c), of one or more curing agents of the type comprising polyphenols and/or oligophenols which contain not less than 3 phenolic OH groups and no functional groups of any other type apart from these and e) 0.2 to 3.0% by weight, based on the sum of the epoxide resins listed under a) to c), of one or more curing accelerators and, if desired, additionally f) conventional assistants and additives for lacquers, wherein the said mixture is in the form of a powder, the individual particles being homogeneous particles of the total mixture, and does not contain any epoxide resins listed under a), b) and c) which are liquid or any solvents, or contains liquid epoxide resin and/or solvents only in amounts such that the powder is non-tacky and free-flowing.

10. A mixture according to claim 8, which is composed of a) 10 to 100 parts by weight of one or more epoxide resins which are based on bisphenol A and/or bisphenol F and have an epoxide content of 0.3 to 6.0 equivalents/kg, b) 0 to 100 parts by weight of one or more epoxide resins which are based on phenol novolac or an alkylphenol novolac and have an epoxide content of 3.0 to 6.0 equivalents/kg, d) 15 to 30% by weight, based on the sum of the epoxide resins listed under a) and b), of one or more curing agents of the type comprising polyphenols and/or oligophenols which contain not less than 3 phenolic OH groups and no functional groups of any other type apart from these and e) 0.2 to 3.0% by weight, based on the sum of the epoxide resins listed under a) and b), of one or more curing accelerators and, if desired, additionally f) conventional assistants and additives for lacquers, and wherein the said mixture is in powder form, the individual particles being homogeneous particles of the total mixture, and does not contain any epoxide resins listed under a) and b) which are liquid or any solvents, or contains liquid epoxide resin and/or solvents only in amounts such that the powder is non-tacky and free-flowing.

11. A mixture according to any of Claims 8 to 10, which is suspended in water or in an organic

solvent which does not dissolve the mixture, or in a mixture thereof, the solids concentration being 15 to 50% by weight, based on the total suspension.

12. The use of a mixture according to Claim 1, for the production of acid-resistant, alkali-resistant and ammonia-resistant coatings for metals and other substrates and in particular for steel sheets.

5 13. A mixture according to Claim 1, substantially as hereinbefore described with reference to any of the foregoing Examples. 5

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